



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C11D	A2	(11) International Publication Number: WO 94/03567 (43) International Publication Date: 17 February 1994 (17.02.94)
(21) International Application Number: PCT/US93/06858 (22) International Filing Date: 23 July 1993 (23.07.93) (30) Priority data: 07/924,114 3 August 1992 (03.08.92) US (71) Applicant: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors: WELCH, Robert, Gary; 1187 Madeleine Circle, Cincinnati, OH 45231 (US). BEBOUT, Laurie, Anne, K.; 70 Bent Tree Drive #7D, Fairfield, OH 45014 (US).		(74) Agents: REED., T., David et al.; The Procter & Gamble Company; 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US). (81) Designated States: AU, BR, CA, CZ, JP, KR, PL, SK, Eu- ropean patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: PARTICULATE LAUNDRY DETERGENT COMPOSITIONS WITH POLYVINYL PYRROLIDONE (57) Abstract A detergent additive for inclusion in a particulate, free-flowing laundry detergent composition comprising polyvinyl pyrrolidone, finely divided powder, hydrating salt, and binding agent is presented. A process for making a particulate, free-flowing laundry detergent composition is also presented.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NE	Niger
BE	Belgium	GN	Guinea	NL	Netherlands
BF	Burkina Faso	GR	Greece	NO	Norway
BG	Bulgaria	HU	Hungary	NZ	New Zealand
BJ	Benin	IE	Ireland	PL	Poland
BR	Brazil	IT	Italy	PT	Portugal
BY	Belarus	JP	Japan	RO	Romania
CA	Canada	KP	Democratic People's Republic of Korea	RU	Russian Federation
CF	Central African Republic	KR	Republic of Korea	SD	Sudan
CG	Congo	KZ	Kazakhstan	SE	Sweden
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovak Republic
CM	Cameroon	LU	Luxembourg	SN	Senegal
CN	China	LV	Latvia	TD	Chad
CS	Czechoslovakia	MC	Monaco	TG	Togo
CZ	Czech Republic	MG	Madagascar	UA	Ukraine
DE	Germany	ML	Mali	US	United States of America
DK	Denmark	MN	Mongolia	UZ	Uzbekistan
ES	Spain			VN	Viet Nam
FI	Finland				

PARTICULATE LAUNDRY DETERGENT COMPOSITIONS
WITH POLYVINYL PYRROLIDONE

5

TECHNICAL FIELD

The present invention relates to a detergent additive for inclusion in a particulate, free-flowing laundry detergent composition, comprising: polyvinyl pyrrolidone of molecular weight from about 1,000 to about 100,000, finely divided powder having a particle size of less than about 20 microns, hydrating salt, and binding agent.

Also included is a process for making a free-flowing, particulate laundry detergent composition, comprising forming a detergent additive by mixing the PVP, finely divided powder and hydrating salt, and spraying on the binding agent, and then admixing the additive with detergent particles.

20

BACKGROUND OF THE INVENTION

Polyvinyl pyrrolidone (PVP) is a desirable laundry detergent ingredient because it: (a) inhibits dye transfer in the wash, thus protecting fabric colors; (b) scavenges chlorine from the wash water, thus reducing fabric bleaching by chlorine-containing wash water; and (c) prevents soils released from the washed fabrics from being redeposited on the fabric during the wash. However, it has been found that simply admixing PVP into a granular laundry detergent composition, particularly one containing citric acid, can cause flow problems and lumping and caking over time when the detergent composition is exposed to humid conditions. In the extreme case, the sticky PVP can cause the detergent composition to form into a brick-like mass inside the detergent carton.

It has now been found that this negative effect from admixing PVP into the detergent composition is reduced or eliminated through use of the present PVP additive.

35

Another advantage of this additive involves reducing the problems associated with handling PVP itself in bulk. Bulk

quantities of the additive will tend to cake less and flow better than PVP by itself. It is thus more easily handled.

U.S. Patent 3,868,336, Mazzola et al, issued February 25, 1975, discloses a process for improving flowability of particulate detergents which include an oily detergent improver using a porous
5 or finely divided flow-promoting agent.

U.S. Patent 3,849,327, DiSalvo et al, issued November 19, 1974, discloses the manufacture of a free-flowing particulate heavy duty synthetic detergent composition containing nonionic
10 surfactant and anti-redeposition agent which can be polyvinyl alcohol or polyvinyl pyrrolidone.

SUMMARY OF THE INVENTION

The present invention relates to a detergent additive for
15 inclusion in a particulate, free-flowing laundry detergent composition comprising, by weight of the additive:

- (a) from about 15% to about 60% of polyvinyl pyrrolidone with molecular weight from about 1,000 to about 100,000;
- (b) from about 5% to about 90% of a finely divided powder
20 having a particle size of less than about 20 microns;
- (c) from about 5% to about 60% of a hydrating salt; and
- (d) from about 0.5% to about 30% of a nonionic surfactant.

Also included is a process for making a free-flowing, particulate laundry detergent composition, comprising:

- 25 (1) forming a detergent additive by mixing, by weight of the additive:

- (a) from about 15% to about 60% of polyvinyl pyrrolidone with molecular weight from about 1,000 to about 100,000;
- (b) from about 5% to about 90% of a finely divided powder
30 having a particle size of less than about 20 microns; and
- (c) from about 5% to about 60% of a hydrating salt; and spraying on from about 0.5% to about 30% of a nonionic surfactant; and

- 35 (2) admixing from about 0.1% to about 25% of the particulate detergent additive with from about 99.9% to about 75% of the detergent particles.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is a detergent additive for inclusion in a free-flowing, particulate laundry detergent composition, comprising polyvinyl pyrrolidone, finely divided powder, hydrating salt and binding agent. The additive is preferably also particulate and free-flowing. The ingredients are described below.

Also included is a process for making a free-flowing, particulate laundry detergent composition, comprising forming a detergent additive by mixing PVP, finely divided powder, and hydrating salt, spraying on the binding agent, and then admixing the additive with detergent particles.

Polyvinyl Pyrrolidone

The present detergent additive for inclusion in a free-flowing, particulate laundry detergent composition comprises, by weight of the additive, from about 15% to about 60%, preferably from about 20% to about 50%, most preferably from 25% to 30%, of polyvinyl pyrrolidone with a molecular weight of from about 1,000 to about 100,000, preferably from about 3,000 to about 50,000, more preferably from 5,000 to 30,000, most preferably from 8,000 to 15,000. By "molecular weight" is meant "viscosity average molecular weight", with "K-value" between about 10 and about 34, most preferably between 13 and 19.

PVP in the laundry detergent compositions herein can act as an anti-redeposition agent, a dye transfer inhibitor, and a fabric color protectant. However, simply admixing PVP into a particulate laundry detergent composition can cause flow problems and lumping and caking over time with exposure to a humid environment.

Without meaning to be bound by theory, it is believed that PVP, which is hygroscopic, picks up moisture from the humid air and causes the detergent particles to stick together, thus impeding flow. Further it is believed that PVP-caused stickiness unacceptably increases lumping and caking of the finished detergent product by increasing the force needed to break apart granules bonded by the sticky PVP.

Substituted and unsubstituted vinyl pyrrolidone polymerization products are included herein. Generally, the

higher the molecular weight of the PVP is, the less PVP is needed. Polyvinyl alcohol is preferably not included in the detergent additive and/or the finished detergent compositions herein.

Most preferred is PVP K-15 (ISP) with a viscosity average
5 molecular weight of 10,000 and a K-value of 13-19.

Finely Divided Powder

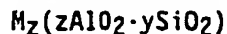
The present detergent additive also comprises, by weight of the additive, from about 5% to about 90%, preferably from about 10% to about 80%, most preferably from 20% to 30%, of a finely
10 divided powder having a particle size of less than about 20 microns, preferably between about 0.1 microns and about 15 microns, most preferably between 1 micron and 10 microns.

By "particle size" is meant average or mean particle size diameter as determined by conventional analytical techniques such
15 as Malvern analysis.

Without meaning to be bound by theory, it is believed that this finely divided powder prevents moisture pick up by the PVP from the air. When the PVP becomes sticky from moisture, the finely divided powder adheres to its surface, preventing
20 interaction between the PVP and the detergent composition.

Preferred finely divided powders herein are selected from the group consisting of calcium carbonate, layered silicate, fumed silica, sodium aluminosilicate, talc, powdered sodium pyrophosphate, and mixtures thereof. More preferred are calcium
25 carbonate, talc, and/or sodium aluminosilicate. Most preferred are calcium carbonate and sodium aluminosilicate, each with a particle size between about 2 microns and about 10 microns.

Preferred aluminosilicates are water-insoluble crystalline or amorphous aluminosilicate ion exchange materials. Preferred
30 aluminosilicates have the formula:



wherein M is sodium, potassium, ammonium or substituted ammonium, z is from about 0.5 to about 2 and y is 1, said material having a magnesium ion exchange capacity of at least about 50 milligram
35 equivalents of $CaCO_3$ hardness per gram of anhydrous aluminosilicate. Aluminosilicates useful herein are commercially available and can be naturally occurring, but are preferably

synthetically derived. A method for producing aluminosilicates is discussed in U.S. Patent 3,985,669. Preferred synthetic crystalline aluminosilicate ion exchange materials herein are available under the designation Zeolite A, X, B, and/or HS. Zeolite A is particularly preferred.

Another suitable finely divided powder is layered silicate. Preferred is a crystalline layered sodium silicate ($\text{Na}_2\text{Si}_2\text{O}_5$), which is available as SKS-6 from Hoechst. Suitable aluminosilicates and layered silicates for use herein are as described in U.S. Patent 5,108,646, Beerse et al, issued April 28, 1992, incorporated herein by reference.

Hydrating Salt

The present detergent additive (which is preferably a "premix") further comprises, by weight of the additive, from about 5% to about 60%, preferably from about 10% to about 50%, most preferably from 20% to 40%, of a hydrating salt. This is preferably selected from the group consisting of the alkali metal salts of carbonate, sulfate, tripolyphosphate, citrate, and mixtures thereof. Sodium (preferred), potassium, or ammonium salts are preferred. By "hydrating salt" is meant alkali metal salts capable of forming one or multiple hydrates over a wide temperature range.

The particle size of the hydrating salts is not limited to small size (eg less than about 20 microns) like the finely divided powder. Preferred are sodium carbonate and sodium sulfate. Preferred particle size (average or mean particle diameter) is from about 1 micron to about 500 microns, most preferably from about 50 microns to about 200 microns.

The preferred ratio of hydrating salt to finely divided powder is from about 1:3 to about 3:1, most preferably about 1:1.

Without meaning to be bound by theory, it is believed that the hydrating salt provides a moisture sink within close proximity to the PVP; therefore, upon exposure of the additive to atmospheric moisture, the salt will first bind the free moisture. In the event the PVP still picks up moisture, it is believed that the finely divided powder will cool the sticky PVP, minimizing interaction with the detergent composition.

Binding Agent

The detergent additive herein further includes, by weight of the additive, from about 0.5% to about 30%, preferably from about 1% to about 20%, most preferably from 3% to 6%, of a binding agent.

The binding agent is preferably selected from the group consisting of nonionic surfactant (preferred), anionic surfactant, water soluble polymers, and mixtures thereof.

Suitable anionic surfactants and water-soluble polymers are as described in U.S. Patent 5,108,646, Beerse et al, issued April 28, 1992, columns 4-7, incorporated herein by reference.

Most preferred are:

- (1) an anionic synthetic surfactant paste or mixtures thereof with ethoxylated nonionic surfactants where the weight ratio of said anionic surfactant paste to ethoxylated nonionic surfactant is at least about 3:1; or
- (2) a water-soluble polymer containing at least about 50% by weight of ethylene oxide or mixtures thereof with ethoxylated nonionic surfactant where the weight ratio of said polymer to ethoxylated nonionic surfactant is at least about 1:1.

The binding agent provides a means to adhere the PVP, finely divided powder, and hydrating salt. It is believed that maintaining the three powders in proximity upon addition to the detergent composition is important herein. This is facilitated by the premixing of the additive ingredients.

The preferred binding agent is a water-soluble nonionic surfactant. Such nonionic materials include compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the polyoxyalkylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Suitable nonionic surfactants include the polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of

alkyl phenols having an alkyl group containing from about 6 to 15 carbon atoms, in either a straight chain or branched chain configuration, with from about 3 to 12 moles of ethylene oxide per mole of alkyl phenol.

5 Included are the water-soluble and water-dispersible condensation products of aliphatic alcohols containing from 8 to 22 carbon atoms, in either straight chain or branched configuration, with from 3 to 12 moles of ethylene oxide per mole of alcohol.

10 Semi-polar nonionic surfactants include water-soluble amine oxides containing one alkyl moiety of from about 10 to 18 carbon atoms and two moieties selected from the group of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of
15 about 10 to 18 carbon atoms and two moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to 18 carbon atoms and a moiety selected from the group consisting of
20 alkyl and hydroxyalkyl moieties of from about 1 to 3 carbon atoms.

Preferred nonionic surfactants are of the formula $R^1(OC_2H_4)_nOH$, wherein R^1 is a C_{10} - C_{16} alkyl group or a C_8 - C_{12} alkyl phenyl group, and n is from 3 to about 80.

Particularly preferred is a condensation product of C_{12} - C_{15}
25 alcohol with from about 2 to about 20 moles of ethylene oxide per mole of alcohol, e.g., C_{12} - C_{13} alcohol condensed with about 6.5 moles of ethylene oxide per mole of alcohol.

The preferred ratio of nonionic surfactant to finely divided powder is from about 1:15 to about 1:2, preferably from about 1:7
30 to about 1:4.

Preferably no additional ingredients are added to the detergent additive, which is preferably free-flowing, particulate and without phosphate.

Process

35 Also included herein is a process for making a free-flowing, particulate laundry detergent composition, comprising forming a detergent additive by mixing the PVP, finely divided powder, and

hydrating salt herein, spraying on the binding agent, and then admixing the additive with detergent particles.

Included herein is a process for making a free-flowing, particulate laundry detergent composition, comprising:

- 5 (1) forming a detergent additive by mixing, by weight of the additive:
 - (a) from about 5% to about 60% of polyvinyl pyrrolidone with molecular weight from about 1,000 to about 100,000;
 - 10 (b) from about 5% to about 90% of a finely divided powder having a particle size of less than about 20 microns; and
 - (c) from about 5% to about 60% of a hydrating salt; and spraying on from about 0.5% to about 30% of a binding agent; and
- 15 (2) admixing from about 0.1% to about 25% of the detergent additive with from about 99.9% to about 75% of the detergent particles.

Mixing is preferably in a: 1) shear mixer (eg kneader, muller), 2) mixer with horizontal movement (eg ribbon mixer, pug mill), 3) turbulent mixer (eg Lodige or Eirich type mixer, pin mixer), 4) high intensity mixer (eg Schugi), or 5) tumble mixer (eg Munson mixer, V-Blender). Preferably, step (1) mixing takes place in a mixer selected from the group consisting of: 1) shear mixers, 2) mixers with horizontal movement, 3) turbulent mixers, 25 4) high intensity mixers, and 5) tumble mixers.

More preferably, mixing is in a turbulent mixer, most preferably a Lodige mixer, or a high intensity mixer, most preferably a Schugi mixer.

Preferably, the order of addition to a batch mixer (e.g. 30 Eirich type mixer) is: powders, most preferably PVP, finely divided powder, and then hydrating salt; followed by liquids, most preferably the binding agent. In a continuous mixer such as a Schugi, the preferred order of addition is: liquids, most preferably the binding agent, being added at the same time that 35 the powders are being added to the mixer.

The detergent additive is then admixed with the detergent particles, preferably on a conveying belt, most preferably in a

rotating tumble mixer. Preferably the order of addition is the detergent particles followed by the additive. Most preferably, the additive is added before any other detergent admixes (such as perfumes, dedusting agents, builders and enzymes).

5 Detergent particles can be prepared by conventional spray drying methods or by agglomeration, most preferably by spray drying. An appropriate agglomeration process is described in U.S. Patent 5,108,646, Beerse et al, issued April 28, 1992, incorporated herein by reference. Appropriate spray drying
10 processes are as described in U.S. Patents 4,963,226, Chamberlain, issued October 16, 1990, and U.S. Patents 3,629,951 and 3,629,955, both Davis et al, issued December 28, 1971. These three are incorporated herein by reference.

Detergent Composition

15 Any conventional granular laundry detergent ingredients can be included herein. Suitable ingredients for use herein are described in U.S. Patents 5,108,646 (see above); 5,045,238, Jolicoeur et al, issued September 3, 1991; and 5,066,425, Ofosu-Asante et al, issued November 19, 1991, all incorporated
20 herein by reference.

The detergent particles which are admixed with the detergent additive preferably comprise, by weight of the detergent particles: from about 1% to about 90% of detergency surfactant, more preferably from about 5% to about 50% of anionic surfactant,
25 most preferably from about 15% to about 30% of sodium alkylbenzene sulfonate and sodium alkylsulfate; from 0 to about 90%, preferably from about 10% to about 70%, of detergency builders, preferably sodium aluminosilicate, sodium silicate, sodium sulfate, and/or sodium carbonate; from about 1% to about 8% of sodium polyacrylate
30 of molecular weight from about 2,000 to about 8,000; from about 0.5% to about 8% of polyethylene glycol of molecular weight from about 4,000 to about 10,000; and from about 0.001% to about 1% of optical brighteners/fluorescent whitening agents.

Additional ingredients are preferably admixed with the
35 detergent particles after the detergent additive. These are preferably from about 1% to about 15% of citric acid, from about 0.5% to about 8% of ammonium sulfate, from about 0.001% to about

1% of protease and/or other enzymes such as amylase, lipase and cellulase, from about 0.01% to about 1% of perfume, and from about 0.001% to about 1% of suds suppressor. The suds suppressor is preferably as described in U.S. Patent 4,652,392, Baginski et al,
5 issued March 24, 1987, which is incorporated herein by reference.

Also included herein is a free-flowing, particulate laundry detergent composition, preferably without phosphate, comprising the above described additive. The free-flowing, particulate laundry detergent composition preferably comprises the additive
10 herein, which is preferably free-flowing and particulate, and from about 1% to about 15%, preferably 5% to 7%, of citric acid. The free-flowing, particulate laundry detergent composition preferably comprises from about 0.1% to about 25%, preferably from about 1% to about 15%, of the additive and from about 99.9% to about 75%,
15 preferably from about 99% to about 85%, of the detergent particles.

More preferably, the finished detergent composition comprises from about 2% to about 6% of the detergent additive, from about 97% to about 79% of the detergent particles, and from about 1% to
20 about 15% of citric acid or other additional ingredients, such as perfumes, dedusting agents, enzymes and/or builders. These can be admixed with the detergent particles before or after (preferably) the premix has been added.

The following examples are given to illustrate the parameters
25 of and compositions within the invention. All percentages, parts and ratios are by weight unless otherwise indicated.

EXAMPLES I-III

Particulate laundry detergent compositions are made as
30 follows. "Base Product" is compared to "PVP Control" for % bulk density loss, cake strength, and compression below. First, a Detergent Base is made by spray drying an aqueous slurry of the following components.

Detergent Base

	<u>Percent By Weight</u>
Sodium C ₁₂ alkylbenzenesulfonate	13.8
Sodium C ₁₄₋₁₅ alkylsulfate	6.0

	Sodium aluminosilicate (Zeolite A)	27.7
	Sodium silicate solids (1.6R)	2.4
	Sodium sulfate	29.0
	Sodium polyacrylate (MW 4500)	3.6
5	Optical brighteners	0.3
	Sodium carbonate	6.2
	Polyethylene glycol (MW 8000)	1.6
	Moisture	8.8
	Miscellaneous inert matter	Balance

10

Additional ingredients are admixed with the Detergent Base in a rotating drum as follows.

	Base Product	PVP Control
15	<u>Percent by Weight</u>	<u>Percent by Weight</u>
	Detergent Base	91.62
	Citric acid	5.0
	Ammonium sulfate	2.0
	Protease/amylase (57 Au/g/	
20	20,000 KNu/g	0.9
	Perfume	0.34
	Suds suppressor*	0.14
	Polyvinyl pyrrolidone	1.0

* 5% silicone in polyethylene glycol per U.S. Patent 4,652,392.

25

EXAMPLE I

Both products are packed in lined cardboard containers and placed for 1 week, 4 weeks and 8 weeks in a room which cycles daily between 70°F (21.1°C) and 90°F (32.2°C) and between 40% and 80% humidity. At the end of each period, physical properties of the products are evaluated (see below).

30

"PVP Control" has significant losses in bulk density and physical properties (i.e. Cake Strength and Compression) overall.

Since most detergent products come with a dosing device (e.g. scoop), this bulk density loss translates to a performance loss. When using a dosing device, the lower bulk density can result in lower than target dosages. Lumping and caking negatively impact

35

the consumer's impression of the detergent product. For cake grades of 10.0 and above, the product is difficult to scoop. In comparison, "Base Product" does not have the loss in bulk density or physical properties seen for "PVP Control".

5

	% Density Loss		Cake Strength		Compression	
	Base	PVP	Base	PVP	Base	PVP
	<u>Product</u>	<u>Control</u>	<u>Product</u>	<u>Control</u>	<u>Product</u>	<u>Control</u>
Initial	0	0	7.8 lbf	7.8 lbf	10 mm	10 mm
10 1 week	0	2.7%	6.6 lbf	9.0 lbf	11 mm	12 mm
4 weeks	4.6%	13.0%	7.6 lbf	11.8 lbf	15 mm	20 mm
8 weeks	5.3%	9.4%	9.0 lbf	12.0 lbf	15 mm	19 mm

15 Cake Strength - force required to break compressed cylinder of detergent composition. 0 is best, ≥ 10 is judged unacceptable after 4 weeks.

Compression - measure of height change when the detergent composition is subjected to a downward force in a fixed cylindrical chamber. 0 is best, maximum is typically 2.0.

EXAMPLE II

20 "Base Product" and "PVP Control" are packed in lined cardboard containers and placed in a constant temperature/humidity room for 1 week, 4 weeks and 8 weeks. Room temperature is held at 80°F (26.6°C) and humidity is held at 60% humidity. As in Example I, "PVP Control" has losses in density and physical
 25 properties (i.e. Cake Strength and Compression) overall.

	% Density Loss		Cake Strength		Compression	
	Base	PVP	Base	PVP	Base	PVP
	<u>Product</u>	<u>Control</u>	<u>Product</u>	<u>Control</u>	<u>Product</u>	<u>Control</u>
30 Initial	0	0	7.8 lbf	7.8 lbf	10 mm	10 mm
1 week	0	0	5.6 lbf	5.6 lbf	10 mm	10 mm
4 weeks	1.0%	2.7%	6.0 lbf	8.8 lbf	10 mm	12 mm
8 weeks	4.6%	7.7%	8.0 lbf	9.0 lbf	12 mm	15 mm

35

EXAMPLE III

"Base Product" and "PVP Control" are packed in lined cardboard containers and placed in the same room used for

Example II. In this case, the products are pulled at 1 week, 2 weeks and 4 weeks. Both products used in this test are prepared using new lots of raw materials. The results from this test confirm the trends observed in Examples I and II.

5

	% Density Loss		Cake Strength		Compression	
	Base	PVP	Base	PVP	Base	PVP
	<u>Product</u>	<u>Control</u>	<u>Product</u>	<u>Control</u>	<u>Product</u>	<u>Control</u>
Initial	0	0	4.8 lbf	3.5 lbf	5 mm	4 mm
10 1 week	4.5%	6.0%	7.2 lbf	7.2 lbf	8 mm	8 mm
2 weeks	14.4%	16.4%	8.5 lbf	9.0 lbf	10 mm	10 mm
4 weeks	15.9%	20.1%	7.5 lbf	10.0 lbf	13 mm	18 mm

Conclusion: As shown in Examples I-III, admixing polyvinyl pyrrolidone into these detergent compositions compromises flow, bulk density and lump/cake properties of the finished product upon storage in warm, humid conditions.

15

EXAMPLE IV

Results from a 4-week storage stability test comparing "PVP Control" to "PVP Premix" (the additive of the present invention) are below. "PVP Premix" is prepared by mixing 4% polyvinyl pyrrolidone additive as described below with 96% of the Base Product described in Example I. This composition results in the same level of PVP in finished product for both "PVP Control" and "PVP Premix". Listed below are density loss, cake strength and compression results.

20

25

PVP Premix

30	Polyvinyl pyrrolidone (MW 10,000)	25%
	Sodium carbonate	55%
	Sodium aluminosilicate (Zeolite A)	15%
	Nonionic surfactant*	5%

* C₁₂₋₁₃ alcohol ethoxylated with 6.5 moles of ethylene oxide per mole of alcohol.

35

"PVP Premix" is made by mixing PVP, carbonate, and aluminosilicate in an Eirich mixer followed by spray-on of the nonionic surfactant.

<u>% Density Loss vs Time</u>			
	Detergent	PVP Control	PVP Premix
	<u>Base</u>	<u>Product</u>	<u>Product</u>
Initial	0	0	0
1 week	4.5%	6.0%	1.7%
2 weeks	14.4%	16.4%	13.2%
4 weeks	15.9%	20.1%	14.2%

<u>Cake Strength vs Time</u>			
	Detergent	PVP Control	PVP Premix
	<u>Base</u>	<u>Product</u>	<u>Product</u>
Initial	4.8	3.5	5.0
1 week	7.2	7.2	7.2
2 weeks	8.5	9.0	9.0
4 weeks	7.5	10.0	8.1

<u>Compression (millimeters) vs. Time</u>			
	Detergent	PVP Control	PVP Premix
	<u>Base</u>	<u>Product</u>	<u>Product</u>
Initial	0.5	0.4	0.6
1 week	0.8	0.8	0.7
2 weeks	1.0	1.0	1.0
4 weeks	1.3	1.8	1.1

Conclusion: The PVP premix eliminates the flow (% density loss) and lump/cake negative impact of admixed PVP.

EXAMPLES V-VIII

The "PVP Premix" (additive) of Example IV can be varied as follows:

	<u>Example V</u>	<u>Example VI</u>
Polyvinyl pyrrolidone (MW 10,000)	25%	25%
Sodium carbonate	35%	15%

Sodium aluminosilicate (Zeolite A)	35%	55%
Nonionic surfactant*	5%	5%

* C₁₂₋₁₃ alcohol ethoxylated with 6.5 moles of ethylene oxide per mole of alcohol.

5

	<u>Example VII</u>	<u>Example VIII</u>
Polyvinyl pyrrolidone	25%	25%
Sodium sulfate	35%	15%
Sodium aluminosilicate	35%	55%
10 Anionic surfactant*	5%	5%
* Sodium C ₁₂ alkylbenzenesulfonate		

EXAMPLE IX

15 Particulate, free-flowing laundry detergent compositions with or without PVP premix are described below.

PVP Premix

Polyvinyl pyrrolidone	25%
Sodium carbonate	35%
Sodium aluminosilicate (Zeolite A)	35%
20 Nonionic surfactant*	5%

* C₁₂₋₁₃ alcohol ethoxylated with 6.5 moles of ethylene oxide per mole of alcohol.

The above "PVP Premix" is made as in Example IV. It has a ratio of hydrating agent to finely divided powder of 1:1.

25 A Detergent Base having the following composition is spray dried.

Detergent Base

	<u>Percent by Weight</u>
Sodium C ₁₂ alkylbenzenesulfonate	15.9
30 Sodium C ₁₄₋₁₅ alkylsulfate	4.5
Sodium alkylethoxy sulfate (E 1.0)	2.3
Sodium aluminosilicate (Zeolite A)	31.7
Sodium silicate solids (1.6R)	2.8
Sodium sulfate	12.5
35 Sodium polyacrylate (MW 4500)	4.1
Optical brighteners	0.4
Sodium carbonate	11.4

Polyethylene glycol (MW 8000)	2.1
Moisture	11.8
Miscellaneous inert matter	Balance

5 To the spray dried particles of the Detergent Base in a rotating drum, additional ingredients are admixed as follows.

	Base Product	PVP Premix Control
	<u>Percent by Weight</u>	<u>Percent by Weight</u>
10 Detergent Base	90.22	86.2
Citric acid	7.0	7.0
Sodium perborate monohydrate	1.0	1.0
Protease/amylase (57 Au/g/ 20,000 KNU/G	0.9	0.9
15 Lipase (5,000,000 Lu/g)	0.2	0.2
Cellulase (430,000 CEUu/g)	0.6	0.6
Silicone suds suppressor	0.1	0.1
PVP additive (see Example V)	0.0	4.0
Total	100.0	100.0

20

Both products are packed in lined cardboard containers and placed in a constant temperature/humidity room for 1 week, 2 weeks and 4 weeks. Room temperature/humidity are held at 80°F(26.6°C)/60% humidity.

25

	% Density Loss		Cake Strength		Compression	
	PVP		PVP		PVP	
	Base	Premix	Base	Premix	Base	Premix
	<u>Product</u>	<u>Control</u>	<u>Product</u>	<u>Control</u>	<u>Product</u>	<u>Control</u>
30 Initial	0	0	6.7 lbf	5.9 lbf	5 mm	5 mm
1 week	7.4%	2.7%	9.6 lbf	8.1 lbf	9 mm	7 mm
4 weeks	6.1%	4.4%	9.0 lbf	8.6 lbf	7 mm	9 mm
8 weeks	5.6%	5.2%	10.6 lbf	10.5 lbf	10 mm	10 mm

35 Conclusion: The data shows that the modified additive (PVP premix) formulation delivers the benefits shown in Example IV.

premix prevents the negatives associated with admixing PVP directly to the detergent composition.

5

10

15

20

25

30

35

- 18 -

WHAT IS CLAIMED IS:

1. A detergent additive for inclusion in a particulate, free-flowing laundry detergent composition comprising, by weight of the additive:

- (a) from 15% to 60% of polyvinyl pyrrolidone with molecular weight from 1,000 to 100,000;
- (b) from 5% to 90% of a finely divided powder having a particle size of less than 20 microns;
- (c) from 5% to 60% of a hydrating salt; and
- (d) from 0.5% to 30% of a binding agent.

2. A detergent additive according to Claim 1 comprising, by weight of the additive:

- (a) from 20% to 50%, preferably from 25% to 30%, of polyvinyl pyrrolidone with a molecular weight of from 3,000 to 50,000, preferably from 5,000 to 30,000;
- (b) from 10% to 80%, preferably from 20% to 30%, of a finely divided powder having a particle size of between 0.1 micron and 15 microns, preferably between 1 micron and 10 microns;
- (c) from 10% to 50%, preferably from 20% to 40%, of a hydrating salt; and
- (d) from 1% to 20%, preferably from 3% to 6%, of a binding agent.

3. A detergent additive according to any of the preceding claims wherein the finely divided powder is selected from the group consisting of calcium carbonate, layered silicate, fumed silica, sodium aluminosilicate, powdered sodium pyrophosphate, talc, and mixtures thereof; and the hydrating salt is selected from the group consisting of the alkali metal salts of carbonate, sulfate, tripolyphosphate, citrate, and mixtures thereof.

- 19 -

4. A detergent additive according to any of the preceding claims wherein the binding agent is selected from the group consisting of nonionic surfactant, anionic surfactant, water soluble polymer, and mixtures thereof.
5. A free-flowing, particulate additive according to any of the preceding claims wherein the finely divided powder is selected from the group consisting of calcium carbonate, talc, and sodium aluminosilicate; the binding agent is nonionic surfactant; and the ratio of binding agent to finely divided powder is from 1:15 to 1:2.
6. A detergent additive according to any of the preceding claims wherein the ratio of hydrating salt to finely divided powder is from 1:3 to 3:1; and wherein the nonionic surfactant is a condensation product of C₁₂₋₁₅ alcohol with from 2 to 20 moles of ethylene oxide per mole of alcohol.
7. A detergent additive according to any of the preceding claims wherein the ratio of nonionic surfactant to finely divided powder is from 1:7 to 1:4, the ratio of hydrating salt to finely divided powder is 1:1, and the hydrating salt has a particle size from 50 microns to 200 microns.
8. A free-flowing, particulate laundry detergent composition comprising an additive according to any of the preceding claims.
9. A free-flowing, particulate laundry detergent composition without phosphate and comprising from 0.1% to 25% of a free-flowing, particulate detergent additive according to any of the preceding claims, and from 99.9% to 75% of detergent particles.

- 20 -

10. A free-flowing, particulate laundry detergent composition according to Claim 8 or 9 comprising from 2% to 6% of the additive, from 97% to 79% of the detergent particles, and from 1% to 15% of citric acid.

11. A free-flowing, particulate laundry detergent composition according to Claim 9 or 10 wherein the detergent particles comprise, by weight of the detergent particles: from 1% to 90% of detergency surfactant; from 0 to 90% of detergency builder; from 1% to 8% of sodium polyacrylate of molecular weight from 2,000 to 8,000; from 0.5% to 8% of polyethylene glycol of molecular weight from 4,000 to 10,000; and from 0.001% to 1% of optical brighteners or fluorescent whitening agents.

12. A process for making a free-flowing, particulate laundry detergent composition, comprising:

- (1) forming a detergent additive by mixing, by weight of the additive:
 - (a) from 5% to 60% of polyvinyl pyrrolidone with molecular weight from 1,000 to 100,000;
 - (b) from 5% to 90% of a finely divided powder having a particle size of less than 20 microns; and
 - (c) from 5% to 60% of a hydrating salt; and spraying on from 0.5% to 30% of a binding agent; and
- (2) admixing from 0.1% to 25%, preferably from 1% to 15%, of the additive with from 99.9% to 75% of detergent particles; the detergent particles preferably being made by spray drying or agglomeration.

13. A process according to Claim 12 wherein step (1) mixing takes place in a mixer selected from the group consisting of: 1) shear mixers, 2) mixers with horizontal movement, 3) turbulent mixers 4) high intensity mixers, and 5) tumble mixers.



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁵ : C11D 3/37, 17/06, 11/00, 11/02	A3	(11) International Publication Number: WO 94/03567 (43) International Publication Date: 17 February 1994 (17.02.94)
(21) International Application Number: PCT/US93/06858 (22) International Filing Date: 23 July 1993 (23.07.93) (30) Priority data: 07/924,114 3 August 1992 (03.08.92) US (71) Applicant: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors: WELCH, Robert, Gary; 1187 Madeleine Circle, Cincinnati, OH 45231 (US). BEBOUT, Laurie, Anne, K.; 70 Bent Tree Drive #7D, Fairfield, OH 45014 (US).		(74) Agents: REED., T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US). (81) Designated States: AU, BR, CA, CZ, JP, KR, PL, SK, Eu- ropean patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i> (88) Date of publication of the international search report: 23 June 1994 (23.06.94)
(54) Title: PARTICULATE LAUNDRY DETERGENT COMPOSITIONS WITH POLYVINYL PYRROLIDONE (57) Abstract A detergent additive for inclusion in a particulate, free-flowing laundry detergent composition comprising polyvinyl pyrrolidone, finely divided powder, hydrating salt, and binding agent is presented. A process for making a particulate, free-flowing laundry detergent composition is also presented.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

INTERNATIONAL SEARCH REPORT

Int. onal Application No
PCT/US 93/06858

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C11D3/37 C11D17/06 C11D11/00 C11D11/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 421 664 (ROHM AND HAAS COMPANY) 10 April 1991 see column 3, line 10 - column 6, line 57 see column 9, line 48 - column 10, line 22 ---	1,3,8,9, 12,13
A	EP,A,0 327 927 (HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN) 16 August 1989 see page 2, line 23 - page 4, line 32; examples 1-4 ---	1,3,4,8, 9,12,13
A	EP,A,0 075 818 (BASF AKTIENGESELLSCHAFT) 6 April 1983 see page 4, line 8 - page 9, line 20 -----	1,3,8,9, 12,13

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

28 March 1994

Date of mailing of the international search report

18.04.94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Doolan, G

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 93/06858

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0421664	10-04-91	AU-B- 645501 AU-A- 6326490 JP-A- 4145200	20-01-94 11-04-91 19-05-92
EP-A-0327927	16-08-89	DE-A- 3803630	17-08-89
EP-A-0075818	06-04-83	DE-A- 3138551 DE-A- 3208216 CA-A- 1217301 JP-C- 1605604 JP-B- 2029719 JP-A- 58067798 US-A- 4695397	11-08-83 08-09-83 03-02-87 31-05-91 02-07-90 22-04-83 22-09-87